

Biodegradation of Oil Sludge by Amendment Addition and Landfarming

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ABSTRACT

Refinery tank bottom sludge containing high molecular weight petroleum hydrocarbons and PAH has been a significant disposal issue. CRA has developed a cost-effective method for biodegradation of this sludge by a combination of amendment addition with land farming techniques. The sludge analytical data indicated that the total petroleum hydrocarbon (TPH) content of the sludge was 145,000 mg/kg. PAHs were also present. Bench scale testing was performed to determine maximum TPH and PAH removal attainable by a combination of amendment addition and land farming. The sludge was mixed with clean soil and amendments were added including nutrients, microbial isolates and activated sludge. The results showed that it was possible to attain greater than 95% removal of the TPH and between 50% and 99% removal of the individual PAH compounds. It is planned to use this approach to treat 1.3 million gallons of sludge at the former refinery site.

INTRODUCTION

There are approximately 5000 cubic meters of petroleum laden tank bottom sludge at a former refinery Site. Soil sludge data indicated that the total petroleum hydrocarbon (TPH) content of the sludge was 145,000 = milligrams per kilogram (mg/Kg). The polynuclear aromatic hydrocarbon (PAH) concentration ranged from 360 mg/Kg for naphthalene to 33 mg/Kg for benzo(a)anthracene. Phenanthrene was also present at 320 mg/Kg. The metals present in the soil were arsenic, chromium, copper, nickel, and zinc in 34 mg/Kg, 2800 mg/Kg, 206 mg/Kg, 83 mg/Kg, and 100 mg/Kg, respectively. Landfarming is being considered as a treatment for this sludge. Bench scale testing was performed to determine maximum TPH and PAH removal attainable by landfarming and to optimize the conditions for the treatment.

The objectives of this laboratory study were to gather the data necessary to assess the effectiveness of landfarming remediation at the Site; determine the effective concentration/dosage of nutrients and soil amendments required to complete treatment as expeditiously as possible; and determine the end point (percentage removal) under optimized conditions, using a slurry microcosm tests.

MATERIALS AND METHODS

A sample of sludge and a sample of the soil to be used for landfarming were received at the Conestoga-Rovers & Associates (CRA) Niagara Falls laboratory. Initial characterization of the sludge and of the soil was conducted.

In order to simulate landfarming, soil microcosm tests were set up. Physical mixing and aeration were used to maintain aerobic conditions in the microcosms and to simulate landfarming activities. Activated sludge and microbial isolates were tested for use as a source of inoculum. The sludge was mixed with the soil provided and the following amendments were added:

- i) no additions (biotic control);
- ii) activated sludge;
- iii) nutrients;
- iv) nutrients and microbial inoculum (microbial isolates);
- v) nutrients and activated sludge; and
- vi) nutrients, activated sludge, and sodium azide (abiotic control).

Duplicate microcosms were sacrificed at t=0, t=4 weeks, t=8 weeks, and t=12 weeks and analyzed for residual PAH and TPH.

RESULTS AND DISCUSSION

No petroleum hydrocarbons or PAH compounds were found in the soil. The sludge contained naphthalene, acenaphthylene, acenaphthene, fluorene, anthracene, fluoranthene, pyrene, chrysene and benzo(a)anthracene at between 14 and 86 mg/Kg. It also contained phenanthrene at 1020 mg/Kg. Diesel range petroleum hydrocarbons were present in the sludge at 7530 mg/Kg and petroleum hydrocarbons in the fuel oil numbers 2 and 6 – range were present in the sludge at 19500 mg/Kg and 11300 mg/Kg respectively. The analyses are summarized in Table 1.

After 4 weeks, removal of some of the PAH and a small amount of the diesel range hydrocarbons had occurred in the microcosms treated with nutrients and activated sludge. A smaller amount of PAH and diesel range hydrocarbons were present in the microcosms treated with activated sludge alone. Very little PAH removal and no TPH removal was seen in any of the other treatments. These data are shown in Table 2.

After 8 weeks a greater amount of PAH and TPH removal was observed in all of the treatments. Fluorene and benzo(a)anthracene removal were not observed in any of the microcosms. A small amount of phenanthrene removal was observed in the microcosms that had received activated sludge and nutrients and in the azide treated control but not in any of the other microcosm treatments. Seventy-eight (78) percent of fluoranthene was removed in the microcosms that received soil and water alone and greater than 99 percent of fluoranthene was removed in all the other microcosm treatments. Naphthalene removal was greater than 95 percent in all microcosm treatments except for the azide treated control. Removal of the other PAH compounds was:

- i) 26 percent to 62 percent in the microcosms containing soil and water only;
- ii) 20 percent to 65 percent in the microcosms that received activated sludge;
- iii) 48 percent to 86 percent in the microcosms that received nutrients;
- iv) 46 percent to 96 percent in the microcosms that received nutrients and a microbial inoculum; and
- v) 54 percent to greater than 99 percent in the samples that received nutrients and activated sludge.

TPH removal was:

- i) 32 percent to 72 percent in the samples containing soil and water only;
- ii) 4 percent to 68 percent in the samples that received activated sludge;
- iii) 62 percent to 93 percent in the samples that received nutrients;
- iv) 60 percent to 94 percent in samples that received nutrients and a microbial inoculum; and
- v) 88 percent to 99 percent in samples that received nutrients and activated sludge.

These data are shown in Table 3.

After 12 weeks PAH and TPH removal were again observed in all of the treatments. Fluorene removal was not observed in any of the microcosms however 54 percent of the benzo(a)anthracene was removed in the microcosms that received activated sludge and nutrients.

No benzo(a)anthracene removal was observed in any of the other microcosms. A small amount of phenanthrene removal was observed in the microcosms that had received activated sludge and nutrients and in the azide treated control but not in any of the other microcosm treatments. Eighty (80) percent of fluoranthene was removed in the microcosms that received soil and water alone and greater than 99 percent of fluoranthene was removed in all the other microcosm treatments. Naphthalene removal was greater than 86 percent in all microcosm treatments except for the azide treated control.

Removal of the other PAH compounds was:

- i) 16 percent to 85 percent in the microcosms containing soil and water only;
- ii) 5 to 93 percent in the microcosms that received activated sludge;
- iii) 74 to 99 percent in the microcosms that received nutrients;
- iv) 50 to greater than 99 percent in the microcosms that received nutrients and a microbial inoculum; and
- v) 56 to greater than 99 percent in the samples that received nutrients and activated sludge.

TPH removal was:

- i) <1 to 79 percent in the samples containing soil and water only;
- ii) 38 percent to 84 percent in the samples that received activated sludge;
- iii) 63 percent to 89 percent in the samples that received nutrients;
- iv) 71 percent to 91 percent in samples that received nutrients and a microbial inoculum; and
- v) 95 percent to greater than 99 percent in samples that received nutrients and activated sludge.

These data are shown in Table 4.

At both 8 weeks and 12 weeks some PAH and TPH removal was observed in the azide treated control. It is unlikely that this loss was due to volatilization during the stirring of the microcosms because removal of the most volatile compounds measured in this study was not observed. It would be expected that the lighter PAH such as naphthalene, a two ring PAH, and smaller three ring PAH such as acenaphthylene, acenaphthene and fluorene would be lost if volatilization occurred. However, loss of these compounds from the azide treated controls was not observed. It is possible that the azide suppressed but did not entirely inhibit microbial removal of PAH and TPH. The azide treated controls also received activated sludge, which contains a wide range of microbial material with different resistances to various toxins. It is likely that some of these organisms were not killed by the azide and the removal observed in the azide treated controls was due to microbial activity.

The data show that the addition of nutrients increased PAH and TPH removal. The treatment where nutrients alone were added show good PAH and TPH removal indicating the bacteria were present in either the sludge or the soil that were capable of degrading PAH and TPH. Greater removal was observed in the microcosms where both nutrients and activated sludge were added showing that the addition of a rich source of bacteria improved removal when ample nutrients were available. The addition of activated sludge alone did not greatly increase PAH and TPH removal showing that the addition of bacteria without nutrients was not effective.

The results indicate that it is possible to reach the 7400 mg/Kg TPH clean up target for the sludge. The original sludge sample received contained approximately 38000 mg/Kg TPH. The sludge was mixed with the clean soil in a 1:10 ratio which yielded a mixture that contained approximately 3000 mg/Kg TPH. This level was reduced to approximately 70 mg/Kg in the treatment that received activated sludge and nutrients. Therefore, when the concentration of TPH in the sludge alone not considered, the concentration of TPH in the original sludge would be 700 mg/Kg, which is below the target level.

CONCLUSIONS

- Treatment of 10 percent sludge with 90 percent mineral salts medium in a slurry resulted in the removal of 82 percent and 84 percent of chrysene and benzo(a)anthracene, 59 percent of pyrene was between 16 percent and 23 percent of acenaphthene, acenaphthylene, naphthylene, fluorene, and phenanthrene in 6 weeks. No significant decrease was observed in the concentrations of anthracene or fluoranthene or concentrations of diesel of fuel oil range hydrocarbons.
- When the sludge was mixed in a 1:10 ratio with soil, removal of PAH and TPH occurred.
- Removal was enhanced by the addition of nutrients and further enhanced by the addition of activated sludge as an inoculum source.
- After 12 weeks the microcosms, which had nutrients added showed removal of greater than 99 percent of fluoranthene and anthracene, greater than 95 percent of naphthalene and acenaphthylene, greater than 70 percent of acenaphthene, and pyrene, and less than 1 percent removal of fluorene, phenanthrene, and benzo(a)anthracene. Between 63 percent and 89 percent of TPH fractions were also removed.
- The microcosms which had nutrients and activated sludge added showed some removal of PAH and TPH after only 4 weeks. After 12 weeks, greater than 99 percent of fluoranthene, anthracene, and acenaphthylene had been removed as well as 97 percent of naphthalene, 76 percent of pyrene, and greater than 54 percent of acenaphthene and benzo(a)anthracene. Ten (10) percent of phenanthrene and less than 1 percent of fluorene were removed. Between 95 percent and greater than 99 percent of TPH fractions were also removed.
- These results indicated that the TPH clean up target of 7400 mg/Kg can be attained by landfarming treatment.

TABLE 3**T=8 WEEKS ANALYSIS OF LANDFARMING MICROCOSMS**

Parameter	Units	Soil and Water	Soil, Water and Activated Sludge	Soil, Water and Nutrients	Soil, Water, Nutrients and Inoculum	Nutrients and Activated Sludge	Soil, Water, Nutrients, Activated Sludge and Azide
% Naphthalene Removal	(%)	95.4	95.5	98.5	98.4	97.9	<1
% Acenaphthylene Removal	(%)	53.1	65.2	86.2	95.5	<99	<1
% Acenaphthene Removal	(%)	25.5	38.9	48.1	45.9	53.7	<1
% Fluorene Removal	(%)	<1	<1	<1	<1	<1	<1
% Phenanthrene Removal	(%)	<1	<1	<1	<1	5.3	40.0
% Anthracene Removal	(%)	61.5	49.0	<99	68.1	91.3	52.8
% Fluoranthene Removal	(%)	78.0	<99	<99	<99	<99	<99
% Pyrene Removal	(%)	27.7	19.9	62.3	48.8	74.6	14.6
% Chrysene Removal	(%)	n/a	n/a	n/a	n/a	n/a	n/a
% Benzo(a)Anthracene Removal	(%)	<1	<1	<1	<1	<1	<1
% Diesel Removal	(%)	69.5	67.6	93.0	94.2	98.9	57.1
% Fuel Oil#2 Removal	(%)	71.6	61.3	88.3	85.9	97.5	64.1
% Fuel Oil#6 Removal	(%)	32.1	4.2	61.8	59.7	88.1	61.5

TABLE 4**T=12 WEEKS ANALYSIS OF LANDFARMING MICROCOSMS**

Parameter	Units	Soil and Water	Soil, Water and Activated Sludge	Soil, Water and Nutrients	Soil, Water, Nutrients and Inoculum	Soil, Water, Nutrients and Activated Sludge	Soil, Water, Nutrients, Activated Sludge and Azide
% Naphthalene Removal	(%)	86.6	86.2	94.9	95.5	96.9	<1
% Acenaphthylene Removal	(%)	85.2	92.9	98.5	>99	99.6	<1
% Acenaphthene Removal	(%)	74.6	78.3	73.6	73.0	55.8	<1
% Fluorene Removal	(%)	<1	<1	<1	<1	<1	<1
% Phenanthrene Removal	(%)	<1	<1	<1	<1	9.69	18.7
% Anthracene Removal	(%)	66.3	56.5	>99	>99	>99	<1
% Fluoranthene Removal	(%)	80.4	>99	>99	>99	>99	>99
% Pyrene Removal	(%)	16.3	5.43	78.2	49.8	75.5	41.5
% Chrysene Removal	(%)	n/a	n/a	n/a	n/a	n/a	n/a
% Benzo(a)Anthracene Removal	(%)	<1	<1	<1	<1	54.0	<1
% Diesel Removal	(%)	78.9	84.0	88.5	91.4	99.3	<1
% Fuel Oil#2 Removal	(%)	45.5	61.6	84.9	84.6	98.3	<1
% Fuel Oil#6 Removal	(%)	<1	38.1	63.1	71.4	94.5	9.45